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**INTRINSICALLY SURVIVABLE
STRUCTURAL COMPOSITE
MATERIALS**



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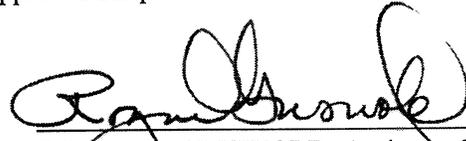
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FOREWORD

This report was prepared by the University of Dayton Research Institute under Air Force Contract No. F33615-95-D-5029, Delivery Order No. 0005. The work was administered under the direction of the Nonmetallic Materials Division, Materials and Manufacturing Directorate, Air Force Research Laboratory, Air Force Materiel Command, with Dr. James R. McCoy (AFRL/MLBC) as Project Engineer.

This report was submitted in December 1999 and covers work conducted from 15 September 1998 through 14 September 1999.

EXECUTIVE SUMMARY

The mixing of nanoscale particles into an aerospace epoxy resin has been accomplished. The complete dispersion of particles was considered the most difficult problem during processing. A combination of mechanical and ultrasonic mixing was found to produce the best results. Agglomeration of nanoparticles occurred in many of the formulations, particularly when the particles started out in suspension.

The particle surfaces could be modified with silane coupling agents. These agents could have either amine or epoxide functionality. Since these same silanes are silica formers, which by themselves produced similar mechanical property changes in the epoxy resin, it is not clear whether the surface modification of the particles is a necessary part of the formulation. When large amounts of the silanes were added, a dramatic decline in the T_g resulted.

While a range of particle mass fractions was made, the best results were obtained with only one-percent spherical nanoparticles. The fracture toughness of this formulation was over twice that of the control resin. Even when the addition of nanoparticles did not increase the average fracture toughness of the resin, it did decrease the spread in the data. Generally the addition of spherical nanoparticles and/or silicate formers had little effect on the flexural strength or stiffness of the resin. Limited layered silicate formulations had no significant effects on fracture toughness but did double the flexural strength and stiffness of the resin.

1. COMPOSITE PROPERTY ENHANCEMENT WITH NANOSCALE FILLERS

Nanoscale-reinforced polymeric composites, or nanocomposites, have been shown to offer tremendous improvements in mechanical and physical properties at very low loading levels for a number of polymeric resins [1-3]. Such low loadings enable conventional polymer processes such as injection molding and potential matrix modifications for fiber-reinforced composites. These attributes can provide affordable performance and/or improved tailorability for many aerospace applications.

It is well established that a number of key parameters dictate the effect of particles on final composite properties, including volume fraction, shape, size/surface area, dispersion, orientation, adhesion or interface, packing, chemical composition, and respective moduli of the filler and polymer. The relationship between the effects of these variables and some properties (e.g., fracture toughness) is often difficult to predict as final behavior may involve a number of either cooperative or competing mechanisms and become quite complex. In general the inclusion of microscale rigid particles into brittle resins tends to lead to increased modulus and toughness and decreased fracture tensile stress and strain [4].

The interfacial surface treatment has also been shown to influence properties, especially the crack initiation energy [5]. The effect of size (and shape) is not well understood, though it has been demonstrated that particle size will affect certain properties [6-7]. Possible explanations of the size effect include: the high specific surface area and increased role of interface and increased surface energy, the relationship between flaws and volume, and the effects of fillers on the cure of the polymer.

2. SPHERICAL SILICATES

This size relationship for spherical particles is pictured in Figure 1. While the relative distances are dependent on the volume fraction, the absolute distances (at a given volume fraction) are dependent on the particle size. The pictured 20-nm particles were the most commonly used silica particles in this section; they give an interparticle distance of only 44 nm which is on the order of the molecular chain dimensions of the epoxy polymer. The face-centered cubic arrangement produces the maximum separation of the particles (along with hexagonal-close packing); therefore other packing arrangements of separated particles produce even closer interparticle separations.

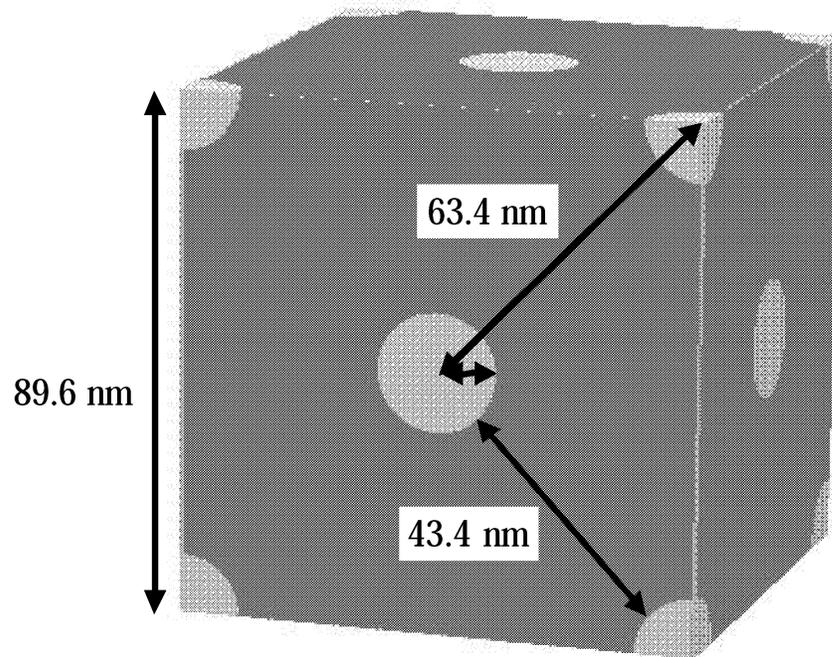


Figure 1. Distances for Spherical Silica Particles (20 nm diameter) in Epoxy at 5% by Weight (2.4% by Volume) in a Face-Centered-Cubic Arrangement.

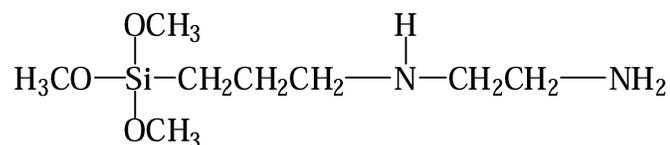
Research has shown unexpected property improvements for nanoscale composites. Going from the micro- to the nanoscale introduces some unique aspects: at the nanoscale, specific surface area is very high (20 nm particles have 250 times the surface area-to-volume

ratio of 5 μm particles), resulting in an increased effect of interface at low filler volumes, and filler size is approaching the scale of the polymer chain. Typical filler trends may or may not hold at these scales [8]. Nanocomposites offer another means for tailoring at the morphological level, which can have a great impact on fracture behavior.

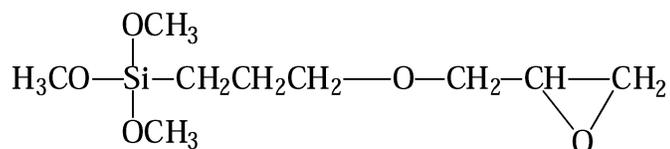
2.1 Experimental

The resin examined in this study was Shell Epon 862 (a bis-phenol F epoxy) and Epi-Cure curing agent W (Cure W, an aromatic amine), a typical aerospace resin that can be resin transfer molded if desired. Silicate particles were obtained from commercial sources as fumed powders (US Silica Min-U-Sil 5: a 5 μm particle and Nanophase NanoTek silicon dioxide: 33 nm particle) or colloidal suspensions (Alfa Aesar: 4 nm particles 15 percent in water and 20 nm particles 40 percent in water). Tetraethyl orthosilicate (TEOS), a silica former, was obtained from Aldrich, as were the Dow Corning coupling agents: Z-6020, N[3-(trimethoxysilyl)propyl]-ethylene diamine (coupling agent A), and Z-6040, 3-glycidoxypropyl trimethoxy silane (coupling agent B). The chemical structures of the silanes are given here:

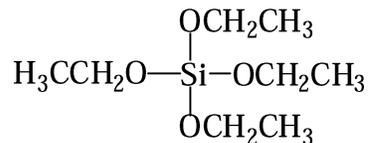
Coupling agent A (Z-6020):



Coupling agent B (Z-6040):



Tetraethyl orthosilicate or tetraethoxysilane (TEOS):



The general chemical reaction of the silanes with water or the hydroxyl groups of the silicate particles to form additional silicate and alcohol is given here:

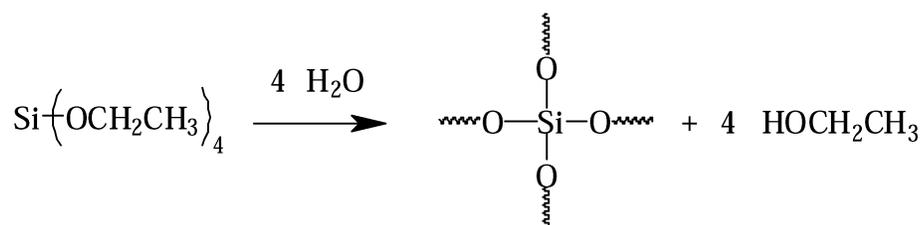


Table 1 lists the nanocomposite panels which were made and tested. Silicate particles were introduced into the resin system in one of several ways. Colloidal water suspensions were mixed with either the epoxy resin or the amine curing agent. Fumed particles were suspended in isopropyl alcohol and then mixed with the epoxy resin. Particles were also formed *in situ* with TEOS or the silane coupling agents mixed with the epoxy and a small amount of water.

The comments in Table 1 explain some of the mixing procedures. The first two samples are listed as “Control” and “Epon 826WW”. Both of these samples contain just the resin with no particles when cured; the latter had water added during the heating and mixing phase which was subsequently removed by pulling a vacuum on the resin to simulate the effects of water removal when the suspension is added. The sample numbers at the beginning of the table (mixing method “S”) start with either a 20N or 00X. 20N refers to using the 20-nm suspended particles; the 00X means no particles were added. The next letter of C or U indicates that coupling agent was added or it was left uncoupled. The next number, either 00 or 05, indicates the weight percent of addition of the particles. Finally, the last two

Table 1
Production Chart of Spherical Particle Nanocomposite Panels

Sample #	Particle size	Particle Level (%)	Silane	Mixing Method	Comments
Control	na		U	S	Resin: Epon 826 and cure W
Epon 862WWW	na		U	S	Resin: water added and removed
20NU05BA	20 nm	5	U	S	Suspended silica added without silane coupling agent
20NC05AA	20 nm	5	A	S	Suspended silica added with silane coupling agent
20NC05AB	20 nm	5	A	S	Bottom precipitated strip from sample above
20NC05BA	20 nm	5	A	S	Silane coupling agent added to Epon but reacted before silica added
20NU05CA	20 nm	5	U	S	Repeat: suspended silica added without silane coupling agent
00XXC00AA	na		A	S	Silane coupling agent only added to Epon
20NC05CA	20 nm	5	A	S	Suspended silica added with silane coupling agent: stabilized with NH4OH
20NC05CB	20 nm	5	A	S	Repeat: suspended silica added with silane coupling agent
00XC00BA	na		A	S	Higher levels of silane coupling agent only added to Epon
00XC00CA	na		A	S	Silane coupling agent and additional silica former (TEOS) added to Epon
00XC00DA	na		A	S	Repeat: silane coupling agent and additional silica former (TEOS) added
00XC00EA	na		A	S	Repeat: silane coupling agent only added to Epon
00XC00FA	na		A	S	Repeat: silane coupling agent only added to Epon
DA990623	20 nm	5	U	U	Repeat: suspended silica added without silane coupling agent
DA990625	na		B	U	Repeat: silane coupling agent only added to Epon
DA990628	20-30 nm	5	B	U	Sb2O5 particles added with silane coupling agent
DA990629	33 nm	1	B	U	Fumed silica nanoparticles added with silane coupling agent
DA990701	20 nm	5	U	U	Repeat: suspended silica added without silane coupling agent
DA990706	5 µm	1	B	U	Fumed silica microparticles added with silane coupling agent
DA990707	20 nm	1	B	U	Suspended silica added with silane coupling agent
DA990709	na		B	U	Silane coupling agent only added to Epon
DA990804-A	33 nm	1	B	U	Repeat: fumed silica nanoparticles added with silane coupling agent
DA990805-B	na		U	U	Repeat of control ultrasonically mixed

Notes: a = uncoupled, A = amine functional silane; B = epoxy functional silane; B = epoxy functional silane; B = mechanically and ultrasonically stirred; U = mechanically and ultrasonically stirred

letters indicate a trial number. Several of the 00XC001 1 are trials of forming the particles *in situ* from silanes as indicated in the comments.

These designations are redundant to some of the columns in the table but those columns are needed to convey that information for the latter half samples. When the ultrasonic mixing was initiated, a new sample numbering system began. The particles and their level are indicated in the columns and comments. The last sample in the table is a new control where ultrasonic mixing was used.

The particle suspension and resin mixtures (either epoxy or amine component) were mechanically stirred while heating to 50 to 60°C. In some cases ultrasonic mixing was included to help disperse the particles as indicated in Table 1. For fumed particles the dry powders were mixed with isopropanol and then the epoxy at 50 to 60°C. The silanes were added to the epoxy mixture, usually mixed with isopropanol. A few drops of water were added to complete the reaction as given above. In all cases the water and/or alcohol were removed by vacuum at temperature. The final component was then added, either the curing agent to the epoxy mixtures or the epoxy to the curing agent mixture. The amine functional silane “A,” used initially, tended to cure in the epoxy before the Cure W was added until the order was changed; so that the dispersion was carried out in the Cure W, and then the epoxy was added after the water and/or alcohol was removed. The epoxy was mixed with the curing agent in the proportion of 397 g of Epon 862 to 103 g of Cure W, the values adjusted to account for the amine or glycidyl groups in the added coupling agent. The resulting systems of resin, curing agent and particles were then cast between glass plates spaced 6.3 mm apart and cured.

The curing consisted of heating up the casting in an oven to 121°C over 30 minutes, holding at temperature for two hours, then heating to 177°C over 30 minutes and holding for

an additional two hours. The plaque was allowed to cool in the oven to ambient. The resulting cured plaque was approximately 25 cm by 25 cm and 6.3 mm thick.

The glass transition temperature was based on the G'' peak of the dynamic mechanical analysis obtained using a Rheometrics Dynamic Spectrometer II at a frequency of 100 rad/sec, a strain of one percent, and a heating rate of 2°C/min. Resin strength, modulus, and strain-to-failure were measured under ambient conditions using a three-point flexure test configuration on an Instron load frame with a crosshead travel of 0.13 cm/min. The samples were tested using a 7.6-cm span (approximate 12:1 span-to-depth ratio) and were 1.3 cm wide. Ten specimens were tested for each resin formulation. Fracture toughness, K_{Ic} , was measured using the standard compact tension specimen described in the ASTM standard E399. The specimen notch was machined with a diamond wafering blade, and the starter crack was initiated by scoring with a razor blade. Ten specimens were tested for each resin formulation. Table 2 shows the results of the mechanical testing.

Scanning electron microscopy was conducted on some of the compact tension fracture surfaces using a Leica 360 field emission gun scanning electron microscope operating at 15 kV. Secondary and backscatter images were obtained.

2.2 Results and Discussion

The three control samples which contained only resin in the cured plaque showed some variation in their final average fracture toughnesses. There was some improvement in the fracture toughness of the neat resin as a result of the ultrasonic mixing, particularly at the lower levels, but the range of variations in the values was too large to say if there were any significant differences. These values are shown in Figure 2.

Table 2
Mechanical Properties of Spherical Particle Nanocomposite Panels

Sample #	Kq (psi*in ^{0.5})	Strength (ksi)	Modulus (Msi)	Failure Strain	Tg (C)
Control	653 (237)	17.9 (1.1)	0.387 (0.012)	0.079 (0.023)	144
Epon 862WW	531 (124)	15.7 (0.7)	0.373 (0.015)	0.061 (0.007)	146
20NU05BA	792 (157)	17.2 (1.6)	0.353 (0.010)	0.091 (0.024)	148
20NC05AA	563 (61)	15.9 (4.0)	0.391 (0.008)	0.056 (0.033)	129
20NC05AB	518 (77)	na	na	na	na
20NC05BA	292 (117)	7 (5.3)	0.363 (0.046)	na	70
20NU05CA	595 (85)	16.5 (2.8)	0.359 (0.019)	0.062 (0.021)	133
00XXC00AA	906 (117)	17.1 (0.3)	0.336 (0.011)	0.105 (0.015)	145
20NC05CA	712 (123)	18.4 (0.6)	0.34 (0.007)	0.078 (0.012)	137
20NC05CB	573 (44)	na	na	na	na
00XC00BA	631 (180)	15.1 (2.9)	0.35 (0.023)	0.05 (0.020)	85, 145
00XC00CA	na	na	na	na	128
00XC00DA	465 (49)	7 (1.5)	0.475 (0.008)	na	71
00XC00EA	967 (58)	17.8 (1.2)	0.408 (0.004)	0.084 (0.023)	132
00XC00FA	979 (71)	17.6 (1.3)	0.412 (0.004)	0.071 (0.032)	131
DA990623	na	na	na	na	144
DA990625	1013 (103)	17.3 (0.2)	0.38 (0.002)	0.084 (0.014)	147
DA990628	1048 (90)	18.1 (0.6)	0.403 (0.007)	0.113 (0.013)	142
DA990629	1424 (138)	17.4 (0.2)	0.384 (0.004)	0.124 (0.019)	146
DA990701	1230 (193)	16.1 (2.3)	0.391 (0.005)	0.067 (0.020)	149
DA990706	898 (73)	16.9 (0.7)	0.38 (0.003)	0.097 (0.018)	149
DA990707	906 (73)	17.1 (0.9)	0.385 (0.004)	0.092 (0.023)	147
DA990709	847 (65)	17.4 (0.2)	0.38 (0.003)	0.111 (0.010)	147
DA990804-A	614 (136)	16.2 (1.6)	0.384 (0.004)	0.076 (0.029)	143
DA990805-B	780 (138)	17.8 (0.3)	0.385 (0.005)	0.121 (0.016)	na

Kq is the fracture toughness determined from compact tension, 10 samples. Strength, modulus, and failure strain are determined from 3-point flex, 10 samples. Values in parentheses are test standard deviations.

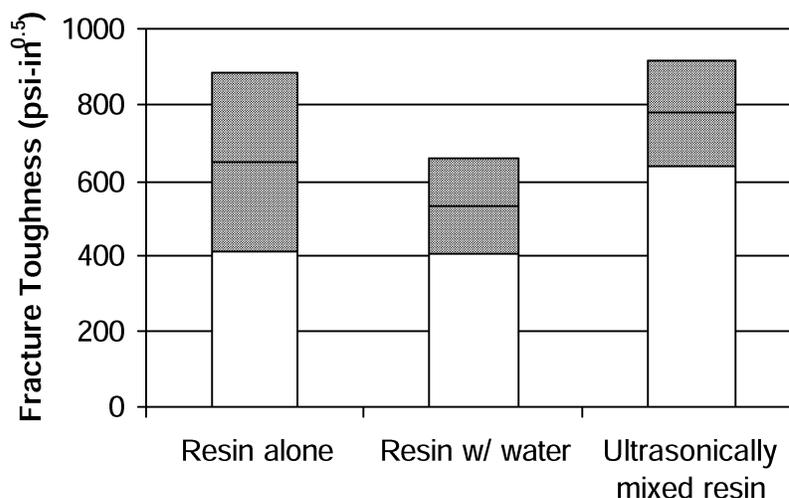


Figure 2. Fracture Toughness Values for the Resin Control Plaques. The diagonals indicate the range of values, converging on the average value.

One interesting result of the mechanical testing was that the variations in results from replicate testing was reduced dramatically when particles were added to the plaques.

The most difficult problem associated with the addition of silica particles to the epoxy resin was the tendency for the particles to fall out of suspension (flocculate). Vigorous mechanical stirring had only a limited ability to disperse the particles in the resin whether the particles were added to the epoxy or the amine component. Heating the reaction flask in an ultrasonic bath resulted in considerably better dispersion than mechanical stirring alone. Higher fracture toughness values were associated with the better dispersion (Figure 3).

The effect of particle size was examined through the use of microscale and nanoscale particles. The suspended 20-nm particles did not produce the fracture toughness improvements expected (Figure 4). This may be a result of poor dispersion of the particles, a function of the fact that the particles start out in suspension, but the original suspension

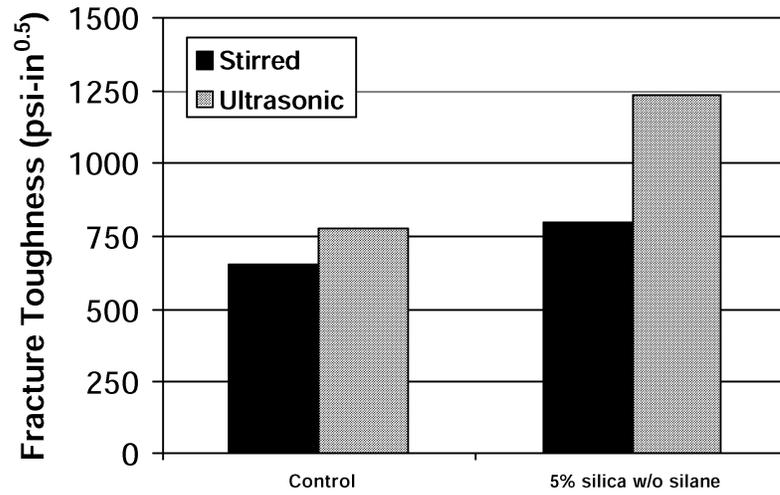


Figure 3. Comparison of the Effect Ultrasonic Mixing has on the Fracture Toughness (Control is Epon Resin Alone).

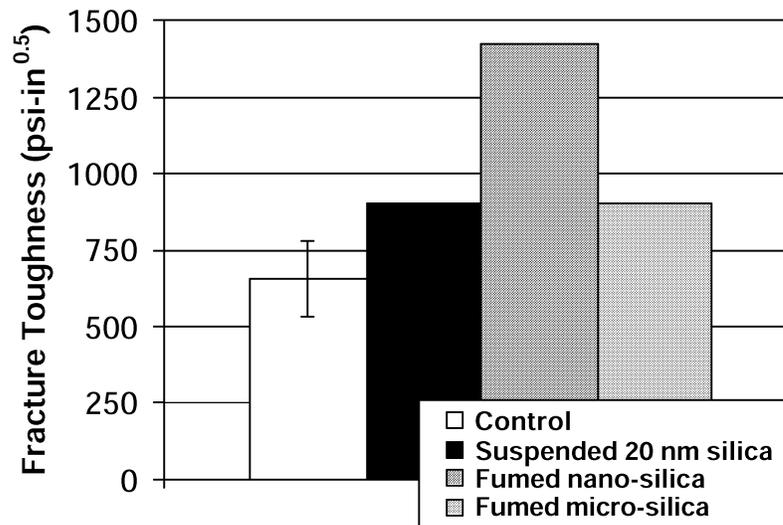


Figure 4. Fracture Toughness of 1% (Weight) Silica of Different Sizes and Origin in the Resin.

media has to be removed while the particles become suspended in the epoxy resin.

Agglomeration of particles was observed in the SEM, with the largest groups resulting when the suspended nanoparticles were used. SEMs of the fumed silica plaque were unavailable, but the agglomeration in the 20- nm suspended particles is seen in Figure 5. The silica domains are hundreds of microns across containing millions of particles. Figure 6 shows a higher magnification of the silica domains where the many nanoscale particles are just visible. Clearly, this agglomeration negates any beneficial effects of the small size of the nanoparticles.

The 5- μm particles produce a small improvement in fracture toughness roughly equivalent to the 20-nm suspended particles which agglomerated. The fumed nanoparticles produce almost twice the fracture toughness of the resin alone (see Figure 4). Flocculation was not observed in the fumed nanosilica, also indicating there was less agglomeration. The fumed nanosilica, on the other hand, start out as dry powders which are suspended in isopropanol which is more easily suspended in the epoxy resin before the alcohol is removed.

Silica weight fractions were varied in the range of 1-5 percent, but increased flocculation was observed at higher silica fractions. Fracture toughness improvements were not as high as expected at higher fractions. Since fracture toughness is very sensitive to morphology, morphological control is very important. Flocculation may be only one culprit, though, as it was observed early that fracture toughness is sensitive to the amount of the silane coupling agent (Figure 7). The effects of silanes as a source of *in situ* particle formers were also observed in this experiment. Figure 7 shows an increase in fracture toughness values as small amounts of silane are added but then a decrease in the fracture toughness values as the amount of silica formers increases.

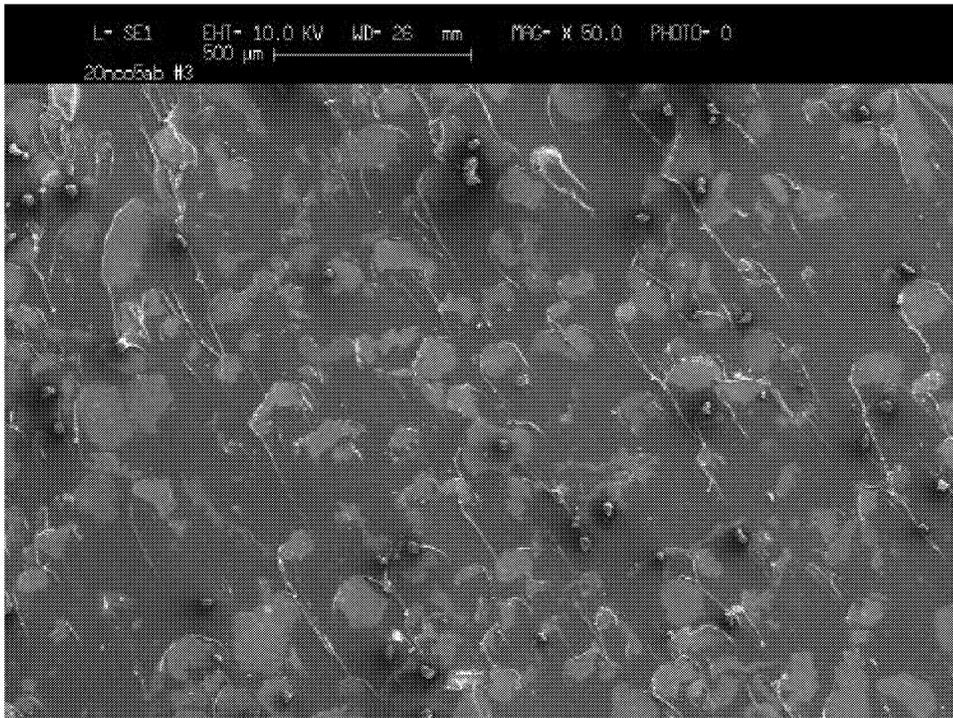


Figure 5. Agglomerated Silica Particles Precipitated from the Suspended 20-nm System Shown in an SEM.

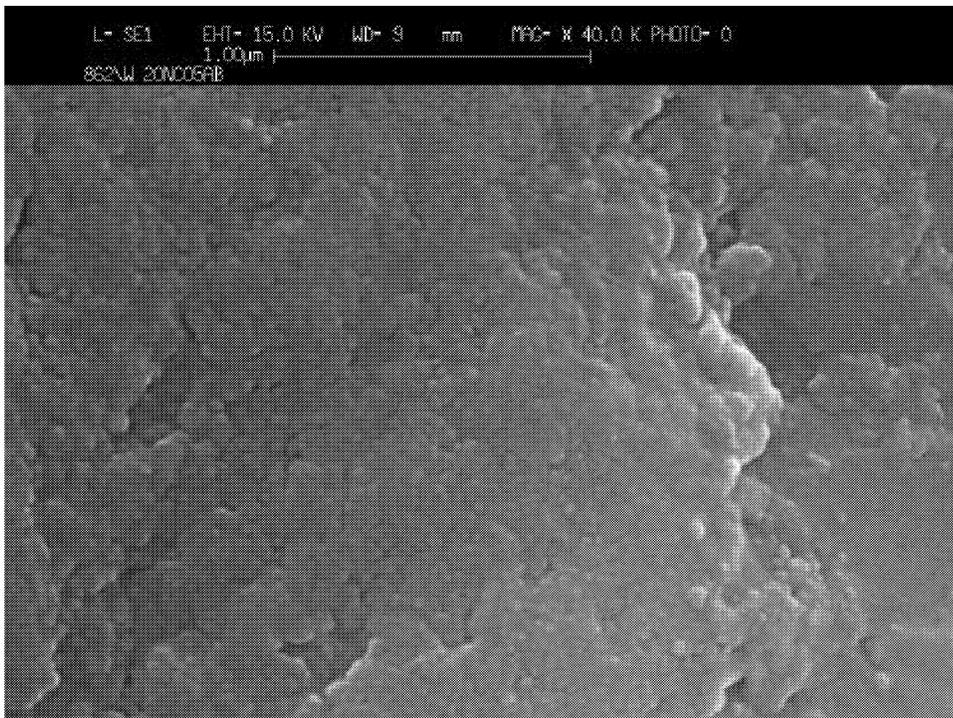


Figure 6. Close-up SEM of the Silica Domains of Figure 5 Showing the Numerous Nanoparticles.

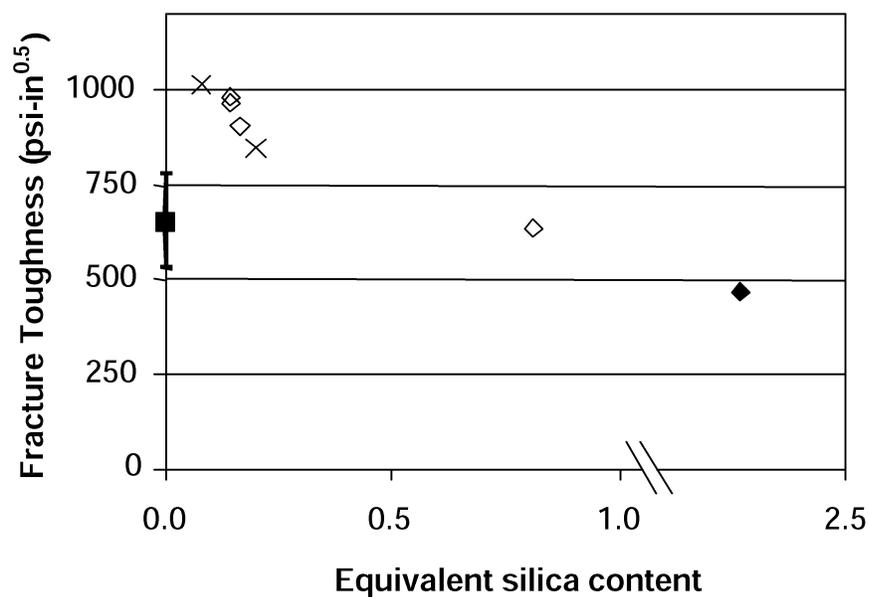


Figure 7. The Addition Silica by *In Situ* Formation of Particles. The solid square is the resin alone, the open diamonds are from silane A, the closed diamond from silane B and TEOS, and the Xs are from silane B alone.

It does not appear that functionality of the organic component of the silane has any appreciable effect on its behavior. The epoxy functional silane (B) fell along the same trend as the amine functional silane (A).

A second issue with the silane observed is the decline in Tg (see Figure 8). The neat resin and resin with particles shows a Tg of $\sim 140^{\circ}\text{C}$. When the amount of silane added rises above 0.8 percent, there is an additional Tg near 71°C . The lower Tg is probably a result of the epoxy polymer chain having links of the more flexible aliphatic groups on the silanes. It is also noted that the fracture toughness improvement with low levels of silane alone is equivalent to the reported improvement for some of the particulate plaques having similar levels of silane coupling agents. The silane alone may be adding the toughness as opposed to the particles.

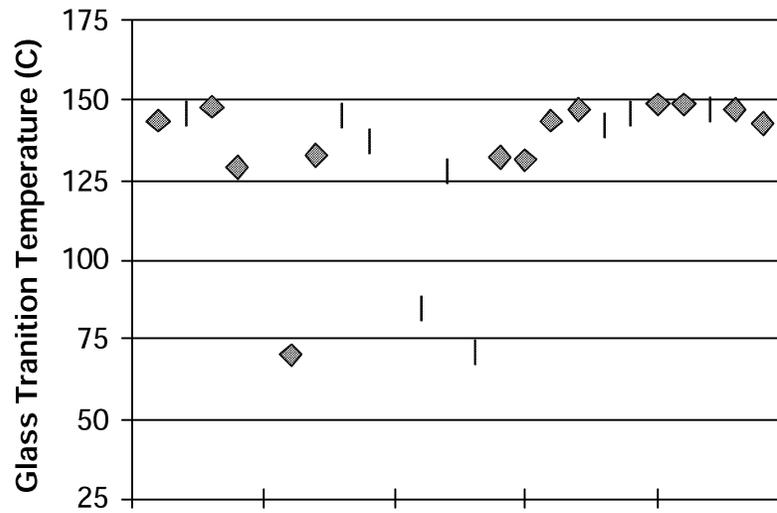


Figure 8. Glass Transition Temperature for the Nanocomposite Plaques Tested.

The flexural strengths and moduli did not change much in most of the plaques. This can be seen in Figure 9. The two low strength points also correspond to samples with low T_g .

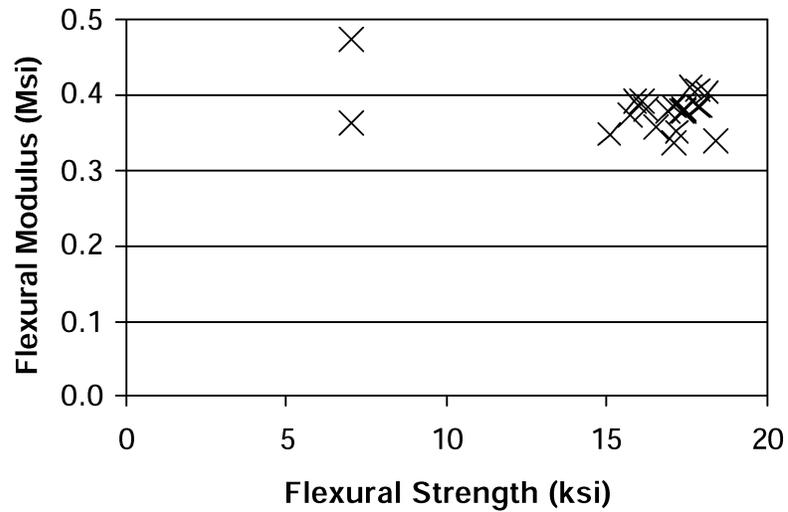


Figure 9. Flexural Properties for all the Plaques Tested.

2.3. Conclusions for Spherical Particles

Nanoscale-filled polymers can produce a significant improvement in an aerospace resin fracture toughness at low volume fractions. However, as fracture toughness is very sensitive to morphology, processing and effective dispersion of these systems is critical. The addition of silane coupling agents to the mixture to improve the interface between silicate particles and resin showed some improvements, but we cannot at this time separate the effects of the silane forming silicate particles from its interface effects.

3. LAYERED SILICATES

Layered nanosilicates are generally produced from natural clays. They have additional property enhancement potentials and processing problems over spherical silicates. The potential as gas barriers is one possible advantage. The additional processing difficulties include the problem of opening up the clay layers (exfoliation) and aligning the layers.

The work to date has been restricted to measuring the mechanical properties of composite resin plaques produced by a Government engineer. The testing techniques were identical to those described for spherical nanoparticle composites. Details of the composition and mixing were not available, but the basic resin was the same as in the spherical nanoparticle work.

Table 3 gives the mechanical testing results for the layered silicate plaques tested. The fracture toughness of the samples did not appear to be affected by the presence of the layered silicates other than the reduction in variability of results (see Figure 10). The flexural strength and modulus were affected (see Figure 11). The modulus was equal to or greater than the control and sometimes more than double that of the neat resin. The strength was sometimes lower than the control but in the higher-modulus samples were about twice the strength of the resin alone.

Table 3
Mechanical Properties of Layered Silicate Nanocomposite Panels

Sample #	Kq (psi*in^{0.5})	Strength (ksi)	Modulus (Msi)	Failure Strain	Tg (C)
DC072899	607 (29)	10.6 (0.3)	0.465 (0.006)	0.025 (0.001)	na
DC081899	496 (77)	28.9 (2.7)	0.788 (0.018)	na	na
DC082099	667 (79)	33.5 (1.7)	0.78 (0.011)	na	na
DC082699	728 (58)	13.7 (0.8)	0.376 (0.004)	na	na

Notes:

Kq is the fracture toughness determined from compact tension, 10 samples.
Strength, modulus, and failure strain are determined from three-point flex, 10 samples.
Values in parentheses are test standard deviations.

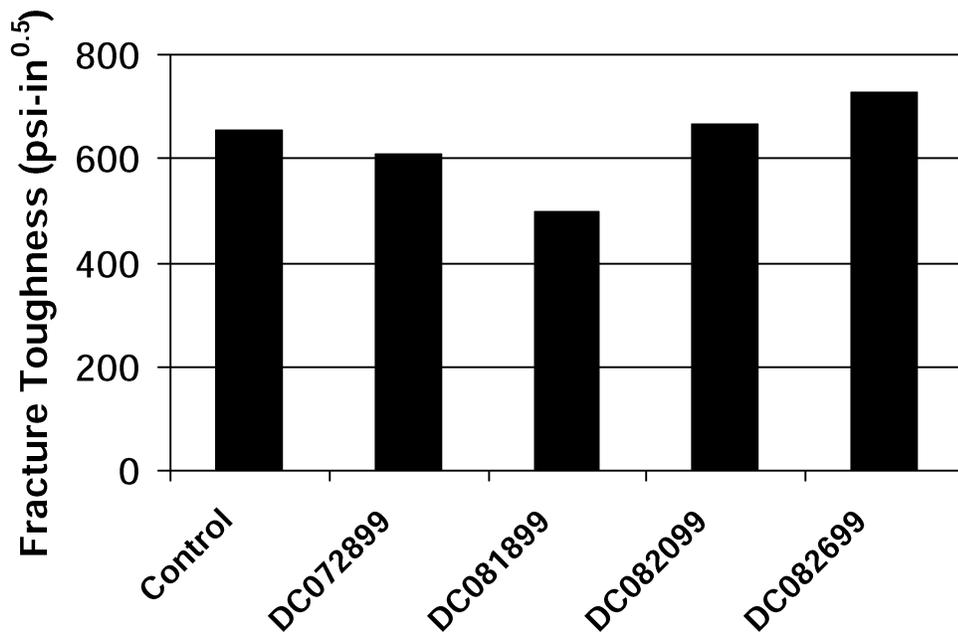


Figure 10. Layered Silicate Fracture Toughness Data.

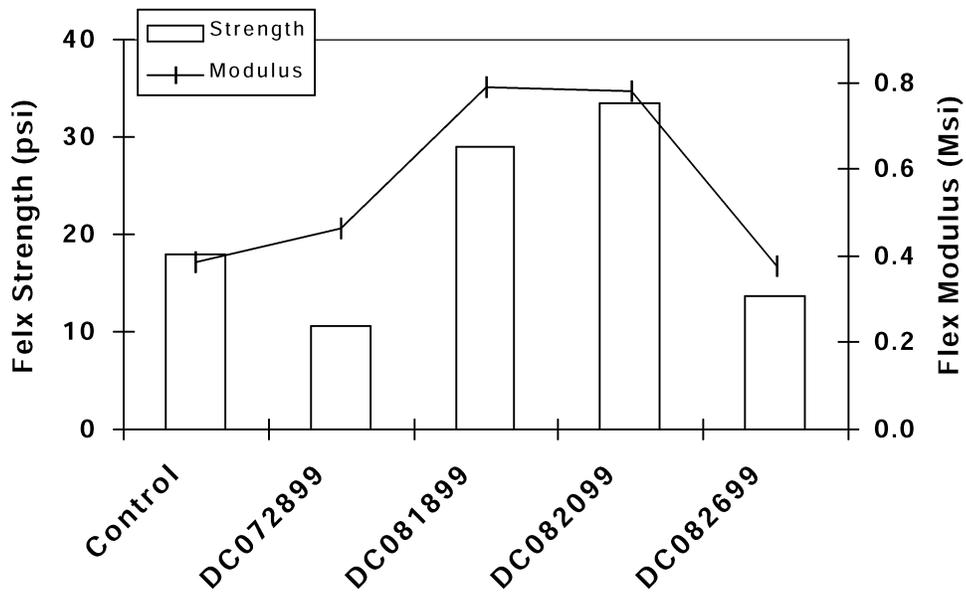


Figure 11. Layered Silicate Flexure Testing Data.

4. PUBLICATIONS

The following publication was generated during this reporting period:

Anderson, D. P., & T. Benson Tolle. (2000). Composite Property Enhancement with Nanoscale Inorganic Fillers. *PMSE Preprints* 82.

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